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The Electronic Structure of Atoms—The Hartree–Fock Method and Correlation*

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On an occasion like the present we should look backward at the earlier stages of our science, and perhaps I may be pardoned for putting more emphasis in this talk on the earlier history of the development of the electronic theory of atomic structure, rather than on the later advances which are familiar to the younger workers in the field. Let me start, then, not merely with the development of Schrödinger's equation in 1926, but six years earlier, in 1920, which happens also to be the year when I started my graduate work, and began to be acquainted with the new atomic theory which was growing up. This was the year, too, in which the *Zeitschrift für Physik* began publication. If a modern reader looks over those early volumes, he will be struck with the many famous papers and famous names which he will find in their pages. Very close to the beginning, we see the first steps toward the modern theory of electronic structure of atoms.

Sommerfeld, several years earlier, in the various editions of his "Atombau und Spektrallinien," which formed the bible for all graduate students of that period, had made it clear that Bohr orbits in a central but non-Coulomb field would lead to energy levels approximately satisfying Rydberg's formula, $E = -1/(n + d)^2$ Rydbergs. No effort had been made to set up a central field leading to actually observed energy levels, however. One of the first such attempts was made by Schrödinger,[1] in an early volume of the *Zeitschrift.* Schrödinger, who in those days before the invention of wave mechanics was just another physicist, tried to investigate Bohr orbits for the valence electron of sodium and showed that the orbit would have to penetrate within the core of the atom, if we assigned to the latter a reasonable radius. At that time, it was not even known what was the principal quantum number of the valence electron, and Schrödinger could not go very far toward finding its value.

The whole picture of the quantum numbers of the electrons in an atom was illuminated in a flash by Bohr's theory of the periodic system of the elements. This theory, first presented in a lecture before the Danish academy, was published in the *Zeitschrift*[2] soon after Schrödinger's paper quoted above, and for the first time we knew that in sodium the 1*s*, 2*s*, and 2*p* orbits were occupied by the inner electrons, while the valence electron was a 3*s*, which could be excited to higher *s* states, or to 3*p*, 3*d*, etc., by absorption of light. The physicist who did not live through that period can hardly imagine the excitement felt by a new graduate student, picking up Number 1 of Volume 9 of the Zeitschrift, and there reading for the first time the complete explanation of the periodic system of the elements. In that paper Bohr made it clear that there must be a central field for sodium in which the inner orbits, corresponding to 1*s*, 2*s*, and 2*p*, lay entirely inside the atom, while the 3*s* orbit was partly outside, partly inside. Obviously it was a matter of the greatest interest to see whether a central field could be found in which the orbits had this behavior, and in which, furthermore, the energy levels of the states matched the experimentally known x-ray and optical energy levels of sodium.

Work was already going on to answer this question, before Bohr's paper came out. Fues[3] and Hartree[4] were trying independently, and by different methods, to work backward from the observed terms to find a potential having the required properties, and each found that it was possible to find the potential, capable of reproducing the energy levels with errors of only two or three percent, and verifying Bohr's assignment of quantum numbers. Hartree stated his potential in terms of a charge distribution which would lead to it and was surprised to find that a smooth continuous distribution of charge was indicated, extending out beyond the radius which we should ordinarily expect for Bohr orbits. This charge distribution was substantially the same which we now know is actually found in the sodium atom, though it was found before wave mechanics, and Hartree checked it by computing x-ray scattering from it, getting results in good agreement with experiment.

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[1] E. Schrödinger, Z. Physik **4**, 347 (1921).

[2] N. Bohr, Z. Physik **9**, 1 (1922).

[3] E. Fues, Z. Physik **11**, 364 (1922); **12**, 1 (1922).

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. **21**, 625 (1923).

Fues and Hartree realized that somehow the charge distribution resulting in this potential must come from the electrons in the atom, but with the current ideas that the electrons moved in sharply defined orbits, it was hard to see how a smooth distribution of the type which they found could be produced from these orbits. This difficulty did not prevent one straightforward attempt to carry through a self-consistent calculation, deriving a charge from a spherical average of the Bohr orbits, and requiring that the orbits themselves be those appropriate to this potential. Such a calculation was carried through, again for sodium, by Lindsay,[5] and it represents the closest approach to a self-consistent field calculation which was attempted on the basis of the old quantum theory.

It is clear from these items of history that Hartree was thinking directly along lines leading to the present self-consistent field method before wave mechanics was invented, and it is not surprising that he was able to propose his method as we now know it very promptly after Schrödinger published his papers regarding wave mechanics in 1926. Hartree's method,[6] reasonable in an intuitive way, of course assumed that each electron moved according to wave mechanics in a central field computed from the nuclear charge, and the spherically averaged charge distributions of all other electrons, and it took essentially a complete form with his first papers. It yielded electronic wave functions, from which the charge distribution in the atom could be found, leading to more accurate checks with charge densities as found by x-ray methods than had been obtained earlier. Also it yielded the energies of the one-electron problems, which showed a close resemblance to the energies of the electrons in the atom, that is, to the negatives of the various ionization potentials, x-ray and optical. At last the suggestion of Bohr was put on a quantitative basis.

The idea of Hartree was almost entirely intuitive in its origin. The first step in fitting it into the wider picture of wave mechanics was taken approximately simultaneously by Gaunt[7] and the present author.[8] They showed that one could set up a many-electron wave function for the atom, as a product of one-electron functions for the various electrons. This function of course was not an exact solution of the many-electron Schrödinger equation. However, each of these authors investigated the nondiagonal matrix components of the Hamiltonian between wave functions, set up in this way for different states of the whole atom, and showed that if the one-electron functions were set up according to Hartree's prescription, the nondiagonal matrix components became smaller than if any other assumption were made for the one-electron functions. This furnished a valid theoretical explanation for the success of Hartree's method.

In addition, these two authors investigated the energy differences between the energy of the complete atom, and of an ion lacking one of its electrons, and showed that these calculated ionization potentials equalled Hartree's one-electron energies (with changed sign), except for small first- and second-order perturbation corrections, which were of the order of magnitude of the errors found in Hartree's calculations. These treatments were an anticipation of the later derivation of the same sort of results from the Hartree–Fock method by Koopmans.[9] As pointed out by both Gaunt and the present author, the corrections are such as to explain the observed fact that the ionization potentials determined by Hartree's method are, in fact, more accurate than the calculated differences between the energies of atom and ion.

Soon after these papers, it occurred to the present author[10] and to Fock[11] that there should be another approach to a demonstration that Hartree's method was a valid application of wave mechanics. If we set up a many-electron wave function as a product of one-electron functions, we should be able to use the variation principle, varying the one-electron functions so as to make the energy stationary. In the two papers mentioned above, it was pointed out that this requirement resulted in equations which were essentially equivalent to Hartree's, differing only slightly, in that they did not include the spherical averaging of the potential which Hartree used.

During the period between the papers of Gaunt and the present author in 1928, and those of the present author and Fock in 1930, our knowledge of the method for handling the requirement of antisymmetry of the wave function had advanced through the suggestion of the present author[12] of the method of combining the determinantal form of the wave function, which had been proposed by Heisenberg[13] and Dirac,[14] with the Pauli treatment of the electron

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[5] R. B. Lindsay, J. Math. and Phys. **3**, 191 (1924).

[6] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89, 111 (1928) and many later papers.

[7] J. A. Gaunt, Proc. Cambridge Phil. Soc. **24**, 328 (1928).

[8] J. C. Slater, Phys. Rev. **32**, 339 (1928).

[9] T. A. Koopmans, Physica **1**, 104 (1933).

[10] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[11] V. Fock, Z. Physik **61**, 126 (1930).

[12] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[13] W. Heisenberg, Z. Physik **38**, 411 (1926); **39**, 499 (1926); **41**, 239 (1927).

[14] P. A. M. Dirac, Proc. Roy. Soc. (London) **A112**, 661 (1926).

spin,[15] to give the determinantal method as we now know it. Before that time, the more cumbersome group-theoretical methods based on the permutation group[16] formed the only method of treating the symmetry of wave functions. These earlier methods were used by Gaunt and the present author in their 1928 papers.

In the 1930 papers of the present author and of Fock, it was realized that the simple product wave function, which was assumed in the derivation of Hartree's equations, was not correct as far as symmetry was concerned, and that Hartree's equations should properly be replaced by more complicated ones arising by the application of the variational method to a properly antisymmetrized combination of one-electron functions. The present author did not set up these more complicated equations, since his main purpose was to show that Hartree's original method was a good approximation to the correct procedure. Fock did set up the more elaborate formulation now known as the Hartree–Fock method, but since he was not familiar with the determinantal method, he used the more difficult techniques of the permutation group, thereby making his paper quite complicated to read. The simplification arising from deriving the Hartree–Fock equations from a determinantal wave function was emphasized by Hartree,[17] when he came to formulate the method for actual calculation.

The work which we have been describing all assumed that the one-electron functions were to be determined by numerical integration of a radial differential equation, the results being presented as tables of values. Very early, however, it was realized that for many purposes it was desirable to have the functions approximated in an analytical way. Among the earliest papers along these lines were those of Guillemin and Zener,[18] and of Eckart,[19] in 1930. Frenkel had earlier included in his textbook on wave mechanics an example of the variation principle, in which the wave function of the helium atom was written in the simple form $e^{-a(r_1+r_2)}$, a function which of course forms the starting point of Hylleraas's treatment of helium, and Frenkel had varied the parameter a to minimize the energy, resulting as is well known in a fairly good approximation to the helium wave function. Guillemin and Zener, in the paper quoted above, extended this method to three-electron atoms, and Zener applied it to the atoms up to neon, arriving at quite acceptable wave functions. The present author[20] used these wave functions of Zener as a basis for suggesting similar analytic wave functions for heavier atoms. This method of analytic approximation to the one-electron functions has been extended from 1930 to the present, with more and more elaborate analytic functions, until the latest beautiful results of E. Clementi (unpublished) for the lighter atoms, and similar results available in various laboratories for heavier atoms, are fully as accurate as the numerical calculations, and are far more desirable for calculation of the various integrals needed in evaluating the energy of the atoms, as well as far better adapted for molecular applications.

From the beginning it was realized that the Hartree and Hartree–Fock methods were of only limited accuracy. The first test of course was in helium, where the error in total energy of the atom, as calculated by the self-consistent field, is nearly 1.5%. As accurate Hartree–Fock calculations have been made for more of the light atoms, for which the experimental energies are known with great accuracy, it has been found that most of the errors run in the neighborhood of a percent. The explanation of the error was straightforward and was understood from the first. The method of the self-consistent field assumes that the various electrons move independently of each other, either completely independently (the Hartree method), or affecting each other only through the requirement of antisymmetry of the wave function (the Hartree–Fock method). On the other hand, it seems intuitively obvious that two electrons, repelling each other by Coulomb repulsion, will be less likely to be found at the same point of space than at points separated from each other. In other words, there should properly be included in the calculation an effect of the correlation of the motion of the various electrons. It has become customary, following the lead of Löwdin, to refer to the energy difference between the Hartree–Fock energy (as corrected for relativistic effects) and the experimental energy as the correlation energy. Obviously the attempt to improve the Hartree–Fock method must be an attempt to include the effect of correlation in the calculation.

Here, the lead has come almost entirely from the work on helium. There are two methods which have proved particularly fruitful for including a correla-

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[15] W. Pauli Jr., Z. Physik **43**, 601 (1927).

[16] E. Wigner, Z. Physik **40**, 492 (1926); **40**, 883 (1926); F. Hund, Z. Physik **43**, 788 (1927); W. Heitler, Z. Physik **46**, 47 (1927).

[17] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A150**, 9 (1935).

[18] V. Guillemin, Jr., and C. Zener, Z. Physik **61**, 199 (1930); C. Zener, Phys. Rev. **36**, 51 (1930).

[19] C. Eckart, Phys. Rev. **36**, 878 (1930).

[20] J. C. Slater, Phys. Rev. **36**, 57 (1930).

tion correction, and both come from the early work of Hylleraas. First[21] is the method now known as configuration interaction. Hylleraas set up, not a single determinantal function, but in principle an infinite set, formed by replacing the one-electron functions, which we now know as spin-orbitals, by any one of a complete set of functions. The resulting complete set of determinantal functions forms a suitable basis set for expressing the true wave function of the problem as a linear combination, and Hylleraas investigated the accuracy of a linear combination of a finite set of determinantal functions, as an approximation to the helium wave function. He realized that the spin-orbitals should include functions belonging to the continuum, if we used Hartree–Fock functions for the excited states as spin-orbitals. To avoid this, he used radial functions formed from Laguerre functions, having the peculiarity that they form a complete set without having any continuum. Hylleraas found a rather slowly-convergent series, which discouraged him from proceeding further with this method. However, Löwdin and Shull[22] have since shown that this method can be easily extended to enough terms to give a quite good approximation to the true wave function of helium. While this is not the best method which we have available for helium, it has been used for some heavier atoms, notably beryllium,[23] where it gives as good results as have so far been obtained for atoms heavier than helium.

The second method for handling correlation, which has proved more successful for the helium problem, was also suggested by Hylleraas,[24] slightly after the paper mentioned earlier. Hylleraas noted that the wave function for the ground state of helium can be regarded as a function of only three variables, r_1, r_2, the distance of the two electrons from the nucleus, and r_{12}, the distance between electrons. It is the dependence on r_{12} which expresses the correlation. He suggested handling this dependence by a procedure which, in its simplest expression, amounts to multiplying a function like $e^{-a(r_1+r_2)}$, the simplest form of product wave function, by a factor like $1 + br_{12}$, describing the way in which the wave function increases with increasing r_{12}. By extending this factor to the form of a series of terms each of which is a product of a power of r_1, a power of r_2, and a power of r_{12}, Hylleraas secured the excellent agreement with experiment with which everyone is familiar.

The use of the term in r_{12} in the wave function has a sound theoretical justification, as was pointed out by the present author[25] in papers appearing before Hylleraas's work. The author pointed out that the true wave function had to depend on r_{12}, in the limit of very small r_{12}, like a factor $e^{\frac{1}{2}r_{12}}$, which of course can be expanded in a power series $1 + r_{12}/2 + \cdots$. This cusplike behavior of the wave function, which increases linearly when one electron moves away from coincidence with the other in any direction, is shown more and more accurately as we get to more and more accurate approximations to the true wave function. The greater success of wave functions employing direct dependence on r_{12}, as compared to the configuration interaction method, arises because in the configuration interaction we are trying to expand this cusplike behavior in Fourier series, a relatively slowly-convergent expansion.

This method of including r_{12} explicitly in the wave function was very successful for helium, but it has proved a very slow process to adapt it for heavier atoms. This is not a result of difficulties in principle, but of the practical problem that the number of terms that must be handled increases extremely rapidly with increasing numbers of electrons. We still do not have successful examples of the application of the method to atoms heavier than lithium. However, work now in progress using similar methods by O. Sinanoğlu and L. Szasz on beryllium is very hopeful, and leads us to the feeling that by using modern computing methods to their limit, we shall be able to achieve a satisfactory treatment of correlation, for atoms appreciably heavier than helium. Furthermore, study of the empirical correlation energies, at the hands of various present workers in the field, making use of the accurate Hartree–Fock energies of Clementi, is leading to empirical generalizations, showing that the largest terms in the correlation energy seem to come from the interaction of two electrons in the same orbital, but with opposite spins. If such generalizations can be justified by more accurate calculations, the problem of handling correlation energy analytically may prove to be less formidable than has been generally thought. Progress in this field seems to be more rapid now than at any time during the last 40 years, and one may well hope that in a few years we shall have solutions of the atomic problem of adequate accuracy, by which one means errors small compared to chemical binding energies. This is the goal, which has not yet been reached for any case except the two-electron atom and ions, where the brilliant work of Hylleraas pointed the way so many years ago.

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[21] E. Hylleraas, Z. Physik **48**, 469 (1928).

[22] P.O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[23] R. E. Watson, Phys. Rev. **119**, 170 (1960).

[24] E. Hylleraas, Z. Physik **54**, 347 (1929).

[25] J. C. Slater, Phys. Rev. **31**, 333 (1928); **32**, 349 (1928).